

$$[Ca - R_i^+] = \frac{(K_{ca})_i [Ca^{2+}] S_i}{\left\{ 1 + \frac{[H^+]}{K_i} + (K_{ca})_i [Ca^{2+}] \right\}} \quad (9)$$

Total calcium complexation can be calculated from

$$[Ca - R_i^+] = [Ca^{2+}] \{ (K_{ca})_1 S_{1u} + (K_{ca})_2 S_{2u} + (K_{ca})_3 S_{3u} \} \quad (10)$$

where S_{iu} is the free site concentration given by

$$S_{iu(i=1,3)} = \frac{S_i}{\left\{ 1 + \frac{[H^+]}{K_i} + (K_{ca})_i [Ca^{2+}] \right\}} \quad (11)$$

and organic charge (X) can be calculated from

$$X = \sum_{i=1,3} S_{iu} = \sum_{i=1,3} \frac{S_i}{\left\{ 1 + \frac{[H^+]}{K_i} + (K_{ca})_i [Ca^{2+}] \right\}} \quad (12)$$

The electrostatic component of K_i in eqs 11 and 12 can be described by eq 6. The calcium binding constant $(K_{ca})_i$ can be written as a combination of chemical (intrinsic) and electrostatic (coulombic) components. Thus

$$(K_{ca})_i = [(K_{ca})_i]_{\text{Intrinsic}} (K_{ca})_{\text{Coulombic}} \quad (13)$$

$(K_{ca})_{\text{Coulombic}}$ may be calculated using the Boltzmann distribution law

$$(K_{ca})_{\text{Coulombic}} = \exp(-e\psi_{ca}/kT) \quad (14)$$

where ψ_{ca} is the potential experienced by the Ca^{2+} ions as they approach the organic surface. As in the case of proton complexation, the humic surface is assumed to be a double layer, with the calcium ions complexing at the surface of the molecule. The potential, ψ_{ca} , is equated to the surface charge (σ_d) using the P-B equation as described previously. Surface charge (σ_d) is calculated from the specific charge values obtained during the calcium complexation experiments at various free calcium concentrations. The relationship between surface charge and surface potential as described by the P-B equation is severely impacted by the presence of divalent cations (18). At a constant surface charge density, relatively small amounts of divalent ions substantially lower the value of surface potential, about 100 times more effectively than monovalent ions. Figure 2 shows a comparison of the effect of the surrounding medium on potentials near a charged surface. This effect is negligible for calcium complexation at high ionic strength ($I \sim 0.1$), where the concentration of divalent ions (i.e., calcium) is low as compared to the salt concentration. However, for calcium complexation at low ionic strengths ($I \sim 0.01$ or 0.005), the divalent ions will control the potential at the organic surface at relatively low free calcium concentrations. This fact has to be taken into consideration while calculating the surface potential (ψ_d) over the course of calcium complexation studies at low ionic strengths.

The only unknowns left in eq 12 are the three values for $[(K_{ca})_{1-3}]_{\text{Intrinsic}}$, which are obtained by fitting this equation to the experimental calcium complexation data. In most cases, data can be adequately modeled using only one or two of the three sites. The optimal fitting parameters for calcium (i.e., $[(K_{ca})_{1-3}]_{\text{Intrinsic}}$ along with other parameters derived from proton complexation data (i.e., S_1, S_2, S_3 , and $(K_1-K_3)_{\text{Intrinsic}}$)

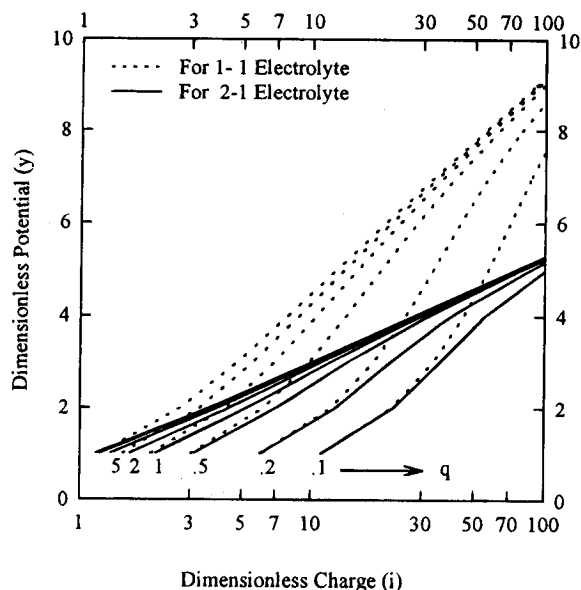


FIGURE 2. Solution of Poisson-Boltzmann equation for 2-1 electrolytes: $y = e\psi/kT$, $i = \sigma/A$, $A = \epsilon kT/\lambda e$, dimensionless distance (q) = κ/λ . Adapted from Loeb *et al.* (16). $T = 298$ K, ϵ (298 K) = dielectric constant of water, 7.08×10^{-12} C V⁻¹ cm⁻¹, $1/\kappa = 0.3(\lambda)^{-0.5}$ nm, at 298 K for 1-1 electrolytes, $1/\kappa = 0.176/[C]^{0.5}$ nm at 298 K for 2-1 electrolytes where $[C]$ is the concentration of 2-1 electrolytes.

TABLE 2. Fitted Model Parameters Describing Proton Complexation of Fulvic Acid

| data set | site concentrations (mequiv/g of C) and equilibrium constants | | |
|--------------|---|-----------------------------|-----------------------------|
| | S_1 | S_2 | S_3 |
| Dempsey (14) | 7.43 | 4.20 | 2.82 |
| Bose (15) | 7.06 | 4.27 | 3.96 |
| data set | $(pK_i)_{\text{Intrinsic}}$ | | |
| | $(pK_1)_{\text{Intrinsic}}$ | $(pK_2)_{\text{Intrinsic}}$ | $(pK_3)_{\text{Intrinsic}}$ |
| Dempsey (14) | 2.09 | 4.26 | 7.69 |
| Bose (15) | 2.11 | 4.27 | 7.3 |

are independent of pH and ionic strength. Hence, they can be used to predict calcium complexation and charge neutralization by calcium complexation at other ionic strengths and pHs.

Results

Proton Complexation. Table 2 and Figure 3 show the modeling results using Dempsey's (14) data. Since no molecular weight or size data were available for this sample, an average molecular weight of 711 was assumed as per ref 19. Parameters were determined from the intermediate ionic strength data, and predictions were made for the high and low sets (i.e., $I = 0.01$ and 1.0). Figure 4 shows a similar model fit and verification for the data set from Bose (15). The average molecular size of the fulvic acid sample used in this case was 1200, as determined by ultrafiltration (15). As with the previous set, the model parameters were determined using only the data for $I = 0.1$ (Table 2). They were then used to predict proton complexation at $I = 0.01$. To help clarify the impacts of ionic strength, predicted values of the conditional proton binding constants are shown in Table 3.

Calcium Complexation. Figure 5 shows the modeling results for calcium complexation at various pH values using Dempsey's data. The intrinsic acidity constants obtained from modeling proton complexation (Table 2) were used.